Studies on the constitution of silicate melts are very important not only in the fields of metallurgical processing or the glass industry, but also in dealing with the properties or constitution of liquids. For this reason a PbO-SiO$_2$ system was chosen as a model of silicate or slag because of its low melting point and glass forming properties.

As a result electrical conductivity measurements, it was found that the lead silicate melt had a positive temperature coefficient and ionic conductance like molten NaCl, which was verified by fused electrolysis. It should be noted that the curves showing the relation between electrical conductivity and composition have breaks at the compounds corresponding to $2\text{PbO} \cdot \text{SiO}_2$ and $\text{PbO} \cdot \text{SiO}_2$. This irregularity was more clearly shown on the curves of activation energy of electrical conductance versus composition. This tendency was also observed in density and viscosity measurements.

The decomposition voltage of the melt was measured by using a Pt anode and molten Pb as a cathode. The electro-motive force of the cell $-\text{Pb}/\text{PbO} \text{(in silicate)}/\text{Pt}: \text{O}_2^+$ was also studied. There was a general decrease of e.m.f. with increasing temperature and concentration of PbO. The activity of PbO in the melts obtained from e.m.f. was compared with values from Richardson's experiments. On the decomposition voltage versus composition curves there are also two breaks at $2\text{PbO} \cdot \text{SiO}_2$ and $\text{PbO} \cdot \text{SiO}_2$.

The differential thermal analysis with the aid of X-ray analysis was conducted in order to find out the mechanism of crystallization of lead silicate glass. The results indicate that even the stoichiometric compounds have different kinds of silicate anion, for example, $2\text{PbO} \cdot \text{SiO}_2$ has $\text{Si}_2\text{O}_7^{6-}$ and others as well as $\text{Si}_4\text{O}_{10}^{4-}$. A new crystal or compound was observed at the composition point corresponding to $3\text{PbO} \cdot 2\text{SiO}_2$, but it was also found that this compound was decomposed to a mixture of $2\text{PbO} \cdot \text{SiO}_2$ and $\text{PbO} \cdot \text{SiO}_2$ above 650°C. The results from the X-ray analysis of lead silicate glass, show that there are three similar groups on the patterns, which coincide with the above mentioned discontinuity on the properties versus composition curves.

1. Introduction

Extensive studies on the crystal structure of minerals have been made by Bragg and his co-workers, but no systematic research has been conducted on the constitution of molten silicates. To get a concrete picture of molten silicates as many methods as possible should be studied, including the measurements of electrical conductivity, density, viscosity and X-ray analysis. Lead silicate usually exists in lead blast furnace slags and causes the main slag loss of lead. In smelting it may be decomposed to lead by metallic iron or diminished to a lower slag content by appropriate slag control methods. Fundamental research on lead silicate melts may be of great importance in the field of fused silicates and metallurgical slags.

2. Experimental Procedure and Results

(a) Measurements of electrical conductivity

The electrical conductivity measurement have been made mainly with respect to metallurgical slag and alkaline glass. Martin and Derge studied the CaO-Al$_2$O$_3$-$\text{SiO}_2$ system. Bockris and his co-workers measured the electrical conductivity of molten silicates with alkali and alkali-earth oxides. Schellinger and Olsen worked on the conductivity of the PbO-$\text{SiO}_2$ system over the temperature range of 730°C to 830°C in silica crucibles. The authors measured the conductivity of the melts ranging from 0 to 60 mol % SiO$_2$ and 800°C to 1150°C in Pt crucibles to avoid contamination of SiO$_2$ from the crucible. The electrode system employed is shown in Fig. 1.

The resistance observed ($R_{\text{observed}}$) showed the following relation, true resistance ($R_{\text{true}}$) and frequency ($\nu$) used.

$$R_{\text{observed}} = R_{\text{true}} + \text{const}/\sqrt{\nu}$$

When 8000 cycle is used as $\nu$, the error was found to be very small. The error introduced from the expansion of the rings used as the electrode was also found to be negligible. Since the resistance of the Pt parts used for the electrode circuit was rather high and tends to increase with temperature, the correction from the total resistance was of course needed. The results are shown in Fig. 2 and Fig. 3.

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(2) A. E. Martin, G. Derge: Trans. AIME, 154 (1943), 104.
The phase diagram of the PbO-SiO$_2$ system is also shown in Fig. 4. The conductivity increased with temperature, and PbO content. There are two breaks on the conductivity-composition curves at compositions corresponding to 2PbO·SiO$_2$ and PbO·SiO$_2$, as shown in Fig. 3. It has been said that there should be the following relation between conductivity ($\kappa$) and temperature.

$$k = A \cdot \exp\left(-\frac{E}{RT}\right)$$

The results obtained by the authors did not confirm this equation, but they were satisfied with the following empirical equation.

$$\log k = -a/T^2 + b$$

As a matter of fact, over a wide temperature range the activation energy ($E$) may not be independent of the temperature. If a narrow temperature range enough to exhibit a linear relation is taken, say 1000°C~1050°C, the activation energy can be calculated from the above equation, which is shown against composition in Fig. 5.

From the above results it may be concluded that PbO-SiO$_2$ melts have an ionic conductance like molten NaCl and even in the liquid state they should be something like compounds in the solid state. The ionic properties of lead silicate melts have been made certain by precipitation of metallic lead at cathode in electrolysis of the fused silicate (of the same sample).\(^{(6)}\) Almost 100% current efficiency has been reached for both PbO·SiO$_2$ and 2PbO·SiO$_2$ melts. During the runs of electrolysis it was also found that the impurities such as Zn, Sn, Sb, and Cd contained in Pb metal react with lead silicate as follows and were eliminated without electric current.

This principle was then applied to crude lead from a smelter and gave satisfactory results as a refining method. (7)

\[
\text{M (in Pb)} + \text{PbO (in silicate)} \rightarrow 
\text{MO (in silicate)} + \text{Pb}
\]

The apparatus used for viscosity measurements is shown in Fig. 7. The oscillating motion is furnished by the handle and logarithmic decrements (\(\delta\)) can be obtained by reading the scale on the aluminium disc. A piano wire of 0.2 mm and a spare brass disc or ring may be changed or added according to the viscosity of the sample. The linear relationship of

\[
v = \Sigma N_i M_i / \rho
\]

where \(\rho\) is the density of the melts, \(N_i\) and \(M_i\) are mole fraction and molecular weight of the component respectively. The curve showing the molar volume thus obtained against composition is shown in Fig. 6. The results indicate that the lead silicate melts have two minimums in the neighborhood of 2PbO·SiO\(_2\) and PbO·SiO\(_2\). The molar volume (\(v\)) of the melts is defined by
The authors first investigated the e.m.f. of the following cell.

\[
\text{Pb/PbO (in silicate)/Pt: O}_2 + \text{O}_2
\]

The construction of the cell with oxygen electrode is shown in Fig. 11. Thermo e.m.f. (about 0.01 V at 850°C) caused by Fe-Pt in the melt should be corrected from the total value to get the true e.m.f. The results are shown in Fig. 12 and Fig. 13. From the e.m.f. values the activity of PbO in silicate can be calculated using the following equation.

\[
-nFE = DF - DF^\circ + RT \ln a_{\text{PbO}}
\]

where \(DF^\circ\) is a standard free energy change of Pb.
(1) + 1/2 \text{O}_2 = \text{PbO}(1)$. Those values against the SiO$_2$ mol \% are shown in Fig. 14.

The decomposition voltage of the silicate melts was measured with almost the same apparatus having a Pt anode and Pb cathode the same as that used for e.m.f. measurements. The results obtained are shown in Fig. 15 and Fig. 16. The decomposition voltage versus composition curves apparently have two breaks at the compound compositions, which were not observed on the e.m.f. values. The calculated values from Richardson's experiments\(^{(21)}\) are also shown for comparison with those of the measurements in Fig. 17.

**Differential Thermal Analysis for Crystalization**

The mechanism of crystalization of lead silicate glass has been investigated by a differential thermal

\[\text{(21) F. D. Richardson, L. E. Webb: Bull. Inst. Min. Metal, 64 (1955), 529.}\]
similar structure to that of the unstable compound, which appears first on the crystallization curve. Before the crystallization starts, heat absorption was observed at the transition temperature in all runs. With the aid of X-ray analysis, the beginning 2SiO$_2$. As a result of further experiments, this compound decomposed to a mixture of 2PbO·SiO$_2$ and PbO·SiO$_2$ above 650°C, so that the phase relation may be drawn by broken lines as shown in Fig. 4.

The X-ray patterns of lead silicate glass are shown in Fig. 19. It can be said that even glassy states have somewhat an ordered structure within a narrow range and this degree seems to become large and the positions of peak on the graph tend to shift toward a large $\theta$ value with increasing PbO content in the glass. The samples containing 28.6 and 33.3 mol% SiO$_2$ exhibit quite similar figures to each other, and the samples of 50.0 and 55.5 mol% SiO$_2$ are almost the same. The glass containing 40.0 mol% SiO$_2$ shows a different type of figure from others.

### 3. Summary

The electrical conductivity, viscosity and density of lead silicate melts have been studied, and the measurements of decomposition voltage of the melts together with the e.m.f. from the cell have been measured and compared with other results. When the various properties of lead silicate melts are plotted against the composition, the curves generally have two breaks, corresponding to 2PbO·SiO$_2$ and PbO·SiO$_2$ respectively, only in the exception of e.m.f.-composition curves. With X-ray patterns of glassy silicates this tendency was also observed. The structural change of the melts seems to occur at these compounds. As a result of differential thermal analysis of 2PbO·SiO$_2$ glass, the crystal of 3PbO·2SiO$_2$ or SiO$_4^6$ appeared first and then 2PbO·SiO$_2$ or SiO$_4^4$ crystallized. It is difficult to predict the mechanism for crystallization from the equilibrium phase diagram only, as seen in Fig. 20.